

Uranium Lung Solubility Class Selection at Bechtel Jacobs Company LLC-Operated Facilities

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INTRODUCTION

Bechtel Jacobs Company LLC (BJC) has been tasked with responsibility for clean-up, decommissioning, and waste management at a number of U.S. Department of Energy (DOE) uranium enrichment and processing facilities. These facilities include gaseous diffusion plants in Paducah, Kentucky; Portsmouth, Ohio; and Oak Ridge, Tennessee; as well as the Oak Ridge Y-12 National Security Complex and the Oak Ridge National Laboratory, both in Oak Ridge, Tennessee. BJC is also responsible for radiological protection of the workers performing the clean-up, decommissioning, and waste management operations at these sites. Respiratory protection and monitoring of inhaled radiological contaminants is based on an understanding of the lung solubility of inhaled radiological contaminants that are present at the site. The DOE Standard *Good Practices for Occupational Radiological Protection in Uranium Facilities* (DOE 2000) recommends that solubility studies be performed to characterize the actual material (e.g., chemical form) present. However, since these sites are massive in area and include hundreds of buildings and other identified facilities or areas, it is not economically or logistically feasible to collect and analyze representative samples from every process area of each site using traditional solubility studies. Therefore, an approach was desired that would focus attention on locations of highest hazard based on the uranium compounds that are known or expected from process history to be present in each facility. In addition, a proper classification of uranium oxides processed at the facilities was desired for purposes of more accurately defining internal exposure potential.

LUNG SOLUBILITY CLASSIFICATION

Inhalation of uranium particles into the lungs results in internal exposure to the radiological (alpha decay emissions) and chemical properties of the uranium. Deposition of particles in the respiratory system is dependent on particle size and on the individuals breathing pattern (mouth or nasal breather). Clearance of the particles may occur through physical processes such as by ciliary motion or by the dissolution of particles in the lung fluid and transportation into the bloodstream. Uranium particles remaining in the lung constitute a potential radiological hazard from the alpha decay energy absorption in the surrounding tissue. Particles that are solubilized into the bloodstream represent a lower radiological hazard, but represent a potential chemical hazard. Therefore, knowing the solubility of uranium particles to which exposure is possible is of importance when determining how to protect workers, with less soluble materials posing a greater radiological exposure hazard. The significance of the radiological hazard is evaluated using models of uptake and removal recommended by national and international scientific radiation protection organizations.

DOE regulations are currently based on the use of the ICRP Publication 30 (ICRP 1979) dosimetric model for the respiratory system. Under this model, materials are classified as D, W, or Y to describe the clearance of inhaled radioactive materials from the lung. These designations refer to the length of time particles from inhaled aerosols are retained in the pulmonary region: D representing days, W representing weeks, and Y representing years. The model takes account of particle sizes within the range of 0.2 Fm to 10 Fm, although 1 Fm Activity Median Aerodynamic Diameter (AMAD) is recommended as the default size. The classifications apply to a range of clearance half-times of less than 10 days for class D, 10 to 100 days for class W, and greater than 100 days for class Y.

ICRP Publication 30 classifies UF₆, UO₂F₂, and UO₂(NO₃)₂ as inhalation class D; UO₃, UF₄, and UCl₄ as class W; and UO₂ and U₃O₈ as class Y. However, ICRP Publication 54 (ICRP 1988) notes that there is evidence from

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animal studies that industrial UO_3 may behave more like a class D material; UF_4 may behave more like a class D material depending on the method used to produce it; and that uranium aerosols from uranium oxide fuel element fabrication may be cleared from the lung with a half-life closer to 100 days than to the 500 days assumed for class Y.

The DOE Standard *Good Practices for Occupational Radiological Protection in Uranium Facilities* (DOE 2000) classifies not only UF_6 , UO_2F_2 , and $\text{UO}_2(\text{NO}_3)_2$ as inhalation class D but also lists $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$, UO_2Cl_2 , UO_2SO_4 , and UO_3 as inhalation class D. It classifies not only UF_4 and UCl_4 as inhalation class W, but also lists U_3O_8 , UO_2 , UO_4 , and $(\text{NH}_4)_2 + \text{U}_2\text{O}_7$ as inhalation class W. It classifies UAl_x , UC_2 , UZr , and only high-fired UO_2 as inhalation class Y. This standard points out that the solubility of the uranium oxides is very dependent on heat treatment and also may be affected by the rate of oxidation.

The lung model described in ICRP Publication 66 (ICRP 1994) classifies the solubility of materials as type F (fast), M (moderate), and S (slow), which broadly correspond to the inhalation classes D, W, and Y of the ICRP Publication 30 system. However, it is assumed that type F is absorbed with a half-time of 10 minutes, that 10% of type M is absorbed with a half-time of 10 minutes and 90% is absorbed with a half-time of 140 days, and that 0.1% of type S is absorbed with a half-time of 10 minutes and 99.9% is absorbed with a half-time of 7000 days. ICRP Publication 66 also uses an improved lung model that better describes deposition, retention, and clearance data and decouples physical and chemical clearance processes. The deposition model is applicable for particle sizes from 0.6 nm to 100 Fm and the default value recommended is 5 Fm AMAD. In spite of these model differences, ICRP Publication 78 (ICRP 1997) suggests that the uranium compounds designated as D, W, and Y by ICRP Publication 30 may be directly correlated to F, M, and S under the new lung model.

LUNG SOLUBILITY STUDIES

Many studies have been conducted by both *in vivo* and *in vitro* methods to report solubility of uranium compounds. The review paper by Eidson (Eidson 1994) provides a large source of references and information regarding the dissolution of uranium. The paper brings together many solubility studies of various uranium compounds. It should be used as a starting point for any review of uranium solubility literature. Other solubility studies are also instructive including those by Mercer (Mercer 1967), Fischhoff (Fischhoff 1965), Heffernan et. al. (Heffernan 2001), Eidson (Eidson 1994), Cook and Holt (Cooke and Holt 1974), Weldon Springs Site Remedial Action Program (Vaughn, 1993), Cusbert et. al. (Cusbert 1994), Metzger (Metzger 1997), The Fernald Environmental Management Project (FEMP) (Soldano 1996), Barber (Barber 1995), and Eckerman and Kerr (Eckerman and Kerr 1999).

In summary, the uranium solubility studies cited above indicate the following conclusions:

- the solubility rate constant (or rate of dissolution) increases rapidly as the particle size is reduced;
- the amount of uranium present in the lung lymph system that builds up from chronic exposure causes solubility half-times to be overestimated when determined from *in vivo* measurements;
- both particle size and heat treatment affect the dissolution rates and make assignment of single solubility classes to compounds difficult;
- studies performed by *in vivo* and *in vitro* measurements show that dissolution rates vary greatly with each chemical species due to differing process history of the material, particle size distributions, specific surface areas, and crystallinity and that insoluble forms may result from oxidation of uranium metal whose surface had slowly oxidized;
- there is an effect on solubility due to the way in which uranium compounds are dried or heat-treated, with the material that was heated the highest temperature being the least soluble; however uranium heated to 540° C only resulted in class D and W dissolution rates;
- typical solubility studies performed by batch dissolution measurements are affected by solution saturation and therefore may be inaccurate.

DISCUSSION

The majority of the uranium at the gaseous diffusion plants is in the form of UF_6 or UO_2F_2 that is produced from process system leaks to the surrounding area. Samples may have been converted to $\text{UO}_2(\text{NO}_3)_2$ prior to

analysis. Therefore, the majority of the uranium found at the gaseous diffusion plants will be in the lung solubility class D. Deposits of UF_4 may also be present in equipment, which would provide the possibility of class W material. However, slow reaction of UO_2F_2 and UF_2 with the atmosphere will provide some possibility of UO_2 and U_3O_8 at the plant site. The possibility of UO_3 , U_3O_8 , UF_4 , and UO_2 exists in the areas where the feed conversion plants were situated at the gaseous diffusion plants or where any waste from the feed conversion plants may be disposed of or stored.

The Y-12 Plant has mainly processed uranium in the form of UO_2 and metal. However, chemical conversions from uranyl nitrate hexahydrate (UNH) to both UO_2 and uranium metal are performed. Although the solubility class for uranium metal is not addressed by the guidance documents, experience at uranium process facilities has shown that uranium metal generally behaves as a class W compound (INEL 1999). However, the possibility of slow oxidation of a significant portion of the surface of the metal to UO_2 and/or U_3O_8 over time must be considered.

From the review of previous solubility studies and the existing guidance documents, it can be concluded that UO_2 exists in two physical forms, depending on heat treatment, and that the solubilities of these two forms are considerably different from each other. Therefore, an understanding of the processes by which UO_2 can be produced is important in determining the appropriate lung solubility classes.

Four processes have produced UO_2 at BJC sites. The first process is the reduction of UF_6 to UO_2 using a calcining process after UF_6 is hydrolyzed to uranyl fluoride and then precipitated with an ammonium solution to ammonium diuranate. This precipitate is filtered or centrifuged, dried, and calcined. The calcination reduces the ammonium diuranate to UO_2 powder. This is an amorphous powder with high a specific surface (surface area per mass ratio) and low density.

The second process is used in recovery operations involving reclamation of uranium waste prior to hydrofluorination and/or metal reduction. The scrap uranium is dissolved in nitric acid solution and thereby converted to UNH. The molten UNH then undergoes a denitration to UO_3 . The UO_3 is reduced to UO_2 by reaction in a countercurrent fluidized bed reactor with either cracked ammonia or hydrogen gas at an elevated temperature (less than $800^\circ C$) prior to being converted in a fluid bed process to UF_4 . This UO_2 is also an amorphous powder with a high specific surface and low density.

A third process involves the production of UO_2 in a sintering (high-fired) process. UNH and UO_3 can be ignited to U_3O_8 in air at 800° to $850^\circ C$ and then reduced to UO_2 at temperatures from 650° to $900^\circ C$. The powders made by these procedures have low densities and large particle sizes (Belle 1961). UO_2 can go through repeated cycles of oxidation ($400^\circ C$) and reduction ($600^\circ C$), but at these temperatures, the specific surface increases. However, when the oxidation temperature is raised to $800^\circ C$, powder sintering occurs, and the resulting UO_2 is unreactive, with a small specific surface (Belle 1961). We conclude that this powder sintering that occurs at $800+^\circ C$ is the appropriate definition of "high-fired" UO_2 that has been designated as solubility class Y by the DOE Standard, *Good Practices for Occupational Radiological Protection in Uranium Facilities*.

The fourth process by which UO_2 may be formed is the oxidation of the uranium metal. The uranium oxide formed in this manner, especially when it is oxidized slowly over time, is very dense with a low specific surface due to the highly dense nature of the original substrate. This process is believed to account for the more insoluble material encountered at the Y-12 Plant after the restart of processes that had been shut down for several years (Eckerman 1999).

We conclude that in the heating and cooling of the sintering process, the UO_2 is organized in its crystal lattice structure, similar to the annealing steel. We also conclude that the UO_2 produced by slow oxidation of the uranium metal has this same crystal lattice structure due to the high density of the metal from which it is produced. UO_2 produced under these conditions is structured as a face centered, cubic compound (Berry and Mason 1959). UO_2 formed by the slow oxidation of uranium metal or high-fired UO_2 has highly ordered or organized crystal lattice. This means that the structure is in its most stable form at the lowest energy.

However, in the calcining or the conversion prior to hydrofluorination and/or metal reduction processes, the UO_2 crystal lattice is mixed with structures that are amorphous. The more amorphous the structure, the more empty spaces there will be in the UO_2 particles due to defects in the crystal lattice. This leads to smaller particles and a

higher specific surface. Higher surface area makes the particles more soluble while the higher ordered lattice structure is less soluble. Therefore, we conclude that only UO_2 produced from sintering at temperatures of $800+^{\circ}\text{C}$ and produced from slow oxidation of uranium metal should be considered lung solubility class Y. All other compounds will be considered as either class D or class W as designated by the DOE Standard, *Good Practices for Occupational Radiological Protection in Uranium Facilities*.

Processes that could produce the “high-fired” class Y UO_2 at any of the BJC facilities include incineration (especially long term such as in the brick or lining of the incinerator), arc welding, powder sintering, and slow oxidation of uranium metal. Since environmental conversion may convert class D compounds to class W, all other processes should conservatively assume class W as the default class to ensure personnel protection.

The Q class definition that has been defined at the Y-12 Plant to represent a mixture of 90% class W and 10% class Y probably represents the circumstance when there is only a thin layer of UO_2 on the surface of uranium metal. It may also provide a reasonable representation of the solubility half-time that has been observed for UO_2 that has not been “high-fired” (approximately 120-140 days) than would the assumed half-time for class W (50 days). However, the use of the ICRP 66 lung model would overcome this contrived compound class since class M assumes 90% of the material has a half-time of 140 days. Under the ICRP 66 lung model, only uranium that is “high-fired” UO_2 or the product of slow oxidation of uranium metal should be classified as class S.

CONCLUSION

Based on the review of guidance documents, solubility studies, and an understanding of the different physical forms that can result when uranium compounds produced by different processes, it is concluded that class W represents an appropriate default lung solubility class for most decommissioning areas where uranium has been handled. Exceptions to this would include:

- where processes could have produced the “high-fired” class Y UO_2 such as incineration (especially long term such as in the brick or lining of the incinerator),
- arc welding, powder sintering (at 800°C or greater), and
- where slow oxidation of uranium metal over time may have occurred.

Many areas may actually contain significant amounts of class D materials. However, use of class W as a default assumption for protection of workers does not create undue operational difficulties with regard to bioassay frequencies and methods or in terms of protective equipment required. However, the using a default assumption of class Y does create difficulties in monitoring programs with being able to detect 100 mrem annually. Therefore, since class D uranium compounds may convert to class W compounds in the environment, but are not likely to convert to class Y solubilities under environmental conditions, BJC intends to use class W as the default uranium inhalation compound class for decisions involving protection of workers at BJC controlled uranium facilities except that class Y will be assumed as the default where the processes listed above are known to be part of the process history of the facility where the workers are located.

Although a Q class definition has been used at the Y-12 Plant in the past, this mixed class was likely due to mixtures of metal and oxidized metal. Since the mixture has been shown to vary depending on the amount of time allowed to oxidize, class Y will be assumed for protection of workers in these metal areas.

The use of process history for defining default solubility class is justified for the following reasons:

- the tasks of performing lung solubility studies on material from each process area would be nearly impossible considering the number of process areas involved at BJC facilities;
- solubility studies are often plagued with inaccuracies due to solution saturation;
- bioassay data from workers in areas where even oxides are handled have generally shown agreement with class W solubility rates unless they are high fired oxides or oxidized metals;
- the processes that produce class Y soluble forms of uranium can be understood and clearly identified; and
- assuming class W for protection against class D solubility compounds does not create undue difficulties in the protection programs and provides appropriate conservatism.

It is important to understand that these assumptions will only be used in making decisions concerning protective measures. In cases of actual measurable exposure, bioassay data will be used to determine appropriate lung solubilities based on excretion rates and/or *in vivo* measurements.

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